Effects of Hurricanes Katrina and Rita on the Chemistry of Bottom Sediments in Lake Pontchartrain, Louisiana, USA

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The effects of Hurricanes Katrina and Rita and the subsequent unwatering of New Orleans, Louisiana, on the sediment chemistry of Lake Pontchartrain were evaluated by chemical analysis of samples of street mud and suspended and bottom sediments. The highest concentrations of urbanrelated elements and compounds (e.g., Pb, Zn, polycyclic aromatic hydrocarbons, and chlordane) in bottom sediments exceeded median concentrations in U.S. urban lakes and sediment-quality quidelines. The extent of the elevated concentrations was limited, however, to within a few hundred meters of the mouth of the 17th Street Canal, similar to results of historical assessments. Chemical and radionuclide analysis of pre- and post-Hurricane Rita samples indicates that remobilization of near-shore sediment by lake currents and storms is an ongoing process. The effects of Hurricanes Katrina and Rita on the sediment chemistry of Lake Pontchartrain are limited spatially and are most likely transitory.

Introduction

Hurricane Katrina made landfall on the U.S. Gulf Coast near Buras, La. (about 75 km southeast of New Orleans), early on Monday, August 29, 2005. Sustained winds during landfall were estimated at 204 km/hr (127 miles per hour), making it a strong Category 3 hurricane; the tidal surge at New Orleans, La., was 3-3.5 m (1). Katrina's effect on New Orleans

(Figure 1) was exacerbated by the city's location on drained wetlands in the Mississippi Delta and by decades of subsidence. Levees protect the city to the north and south, and canals, with the aid of large pumping stations, help drain stormwater from the city. The tidal surge from Hurricane Katrina caused the failure of several levees along the canals, and flooding covered about 75% of the city with a maximum volume of water (2) equivalent to about 7% of the volume of Lake Pontchartrain. Water depths in some neighborhoods reached 3.5 m, and sediment accompanying the floodwaters left extensive mud deposits in some parts of the city. Sediment-laden floodwaters were pumped out of the city, mostly into Lake Pontchartrain, during the following weeks. On September 24, rain and a tidal surge from Hurricane Rita reopened a levee breach on the Inner Harbor Navigation Canal (commonly known as the Industrial Canal), and parts of the city flooded again. Much of this additional floodwater was pumped out during the following week. Potential contamination by inundation of numerous urban contaminant sources (i.e., sewers, sewage treatment facilities, gasoline stations, automobiles, industrial facilities, commercial buildings, and houses), inundation of historically contaminated soils (3), and redistribution of historically contaminated aquatic sediments raised concerns for potential effects on human health in New Orleans and adverse effects on Lake Pontchartrain from floodwaters pumped into the lake.

Lake Pontchartrain is a large, shallow estuary with a surface area of 1630 km² and an average depth of about 4 m. It is connected to the Gulf of Mexico by open channels on the southeast side and the water is brackish. Wind, waves, and tidal fluctuations can resuspend bottom sediment; subsequent sediment redistribution largely is controlled by wind strength and direction (4). Along the south side of the lake, adjacent to New Orleans, sediment transport predominantly is parallel to shore and often to the west, as evidenced on September 13, 2005, by the plume discharging from the Jahncke Canal (Figure 1, zone J). Because water depths are shallow and mixing of relatively fresh canal water and brackish lake water is limited (5), fine-grained sediments discharged from the urban canals could be distributed widely in the lake. Material remaining in suspension ultimately discharges to the Gulf of Mexico.

The objective of this study was to characterize the effect of the discharge of floodwaters from New Orleans on the sediment chemistry of Lake Pontchartrain. Samples of street mud, suspended sediment in canals discharging to the lake, and bottom sediment in the lake were collected and analyzed for numerous constituents. The results are interpreted in this paper in the context of spatial distribution of the constituents in relation to the canals and by comparison to historical data for Lake Pontchartrain, data for other U.S. urban lakes, and sediment-quality guidelines (SQG).

Materials and Methods

The sampling design was based on models of Lake Pontchartain sediment transport and deposition; locations of major canals, pumping stations, and levee breaches; and observations and satellite imagery of sediment plumes in the lake resulting from canal discharges. Sample types and locations were designed to characterize the sources (street mud: four sites), transport (suspended sediment: four sites on canals, one site in the lake (E2), and one site in a flooded neighborhood (CHL)), and fate (bottom sediment in the lake: 27 sites and on canals: two sites) of sediment-associated

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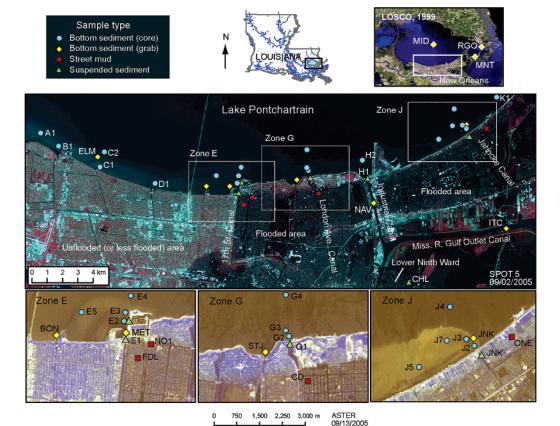


FIGURE 1. Locations of sampling sites in relation to New Orleans and Lake Pontchartrain. Flooded area is darker in upper image. Sediment plumes are visible in the lake and along the shoreline in several images.

Scale and base for bottom three maps

contaminants pumped with floodwater from the city (Figure 1). Site selection focused on three canals that contributed large amounts of floodwater to the lake (Figure 1, zones E, G, and J). Bottom-sediment samples also were collected offshore from other canals, near the middle of the lake (MID), and at the outlet to the Gulf of Mexico (RGO and MNT). Sampling and analytical methods and results are presented in ref 6 and are summarized here. All samples were collected between September 20 and October 21, 2005, after Hurricane Katrina (August 29) and before and after Hurricane Rita (September 24).

Sampling. Street-mud samples were collected from four locations (Figure 1). Sample NO1 was a composite of two 125-mL grab samples collected 1 m apart; the three other samples were composites of nine grab samples collected from approximately 100- by 100-m areas.

Suspended-sediment samples were collected from four canals, from offshore of the mouth of one canal, and from a flooded street in the lower Ninth Ward in southeast New Orleans (Figure 1). The samples were obtained by using a peristaltic pump to transfer water from about 0.3 m below the surface into washed polycarbonate containers. The samples from the mouth of the Metairie Outfall Canal (commonly known as the 17th Street Canal) collected on September 20 (E1 and E2) came from a layer of less saline, low dissolved oxygen water (about 1.0 mg/L) which was assumed to be dominated by canal discharge. Sample volumes ranged from 50 to 140 L. Sediments for elemental analysis were isolated by filtration using $0.45-\mu m$ Teflon filters held in a 140-mm diameter acrylic filter holder (7) or, in two cases, by flow-through centrifugation (8). Sediments for organic-compound analyses were isolated by filtration using 0.45-μm Teflon filters held in a 293-mm diameter stainlesssteel filter holder (7).

Bottom-sediment samples were collected at 19 sites using a 14- by 14-cm², 20-cm tall stainless-steel box corer with a polycarbonate liner, and at 10 sites using a stainless-steel Ekman grab sampler. The surface layer (1–2 cm) was sliced off the top of the box cores using a stainless-steel plate or Teflon-coated spatula. Sediment was transferred to either a glass (for organic analyses) or polycarbonate (for inorganic analyses) jar. At sites E4 and H2, deeper sediments were obtained from box cores by vertically extruding the core and slicing intervals using a stainless-steel plate.

Analytical Procedures. Analytes included radionuclides, major and trace elements, nutrients, polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides, polychlorinated biphenyls (PCBs), current-use pesticides, and urban waste-indicator (UWI) compounds. Analytical methods are presented in ref 6 and references therein and are briefly summarized here.

Freeze-dried sediment samples were analyzed for 210 Pb, 226 Ra, and 137 Cs to estimate sediment accumulation rates and for 7 Be (53.3 day half-life) and 234 Th (24.1 day half-life) as indicators of recent deposition (9) (presumably mostly from floodwaters following the hurricanes). Analyses were done using a high-resolution gamma spectrometer with an intrinsic germanium detector following methods similar to refs 10 and 11. Measured activities of 7 Be and excess 234 Th were decay corrected for the period between September 1 (immediately after Hurricane Katrina) and the date of analysis.

Trace element chemistry was determined on freeze-dried sediment samples digested with hydrofluoric and perchloric acids plus aqua regia in Teflon beakers at 200 °C. Most elements were determined by inductively coupled plasma—atomic emission spectrometry (ICP—AES) following modifications of the procedures of Horowitz et al. (12). Ag, Cd, and Pb were determined from the same digestion by flame

TABLE 1. Selected Chemical Data for Sediment Samples from New Orleans and Lake Pontchartrain^a

site and sample			organic carbon %	lead mg/kg	zinc mg/kg	ΣDDT μg/kg	ΣPCBs μg/kg	Σchlor μg/kg	ΣΡΑΗ _{SQG} μg/kg	paracresol μg/kg	Indole μg/kg	cholesterol μg/kg	Σ fipronil μ g/kg
					7	Zone E—	17th Street	t Canal					
NO1	mud	09/21/2005	4.1	61	250	33	55	24	3 900	<250	440	1 800	E22
FDL	mud	10/03/2005	2.1	170	180	40	84	84	24 000	300	810	E2 300	E30
E1	SS	09/20/2005	7.0	170	2 000	nd	nd	nd	15 000				
E1	SS	10/03/2005		75	640					430	2 900	E74 000	
E2	SS	09/20/2005	6.6	120	840	nd	nd	nd	10 000				
MET	lk sed	09/29/2005	1.1	120	405	23	E680	E81	42 000	620	700	700	E1.9
MET	lk sed	10/03/2005	6.6	210	1 800								
E2 0-2	lk sed	09/21/2005	3.4	200	1 200	E36	E110	E67	12 000	24 000	1 700	4 000	E53
E2 0-1	lk sed	10/09/2005	1.8	70	380	19	55	32	4 700	<250	540	E4 800	
E3 0-2	lk sed	09/21/2005	8.5	71	290	160	710	270	4 000	<250	350	4 000	E27
E3 0-2	lk sed	10/09/2005	4.3	86	650	20	48	40	4 000	490	580	E7 300	
E4 0-1	lk sed	09/21/2005	4.3	53	230	7.7	52	13	1 500				
E4 0-2	lk sed	10/09/2005	3.0	38	150	nd	E6.7	E5.8	1 000	<250	720	E3 900	
E5 0-2	lk sed	10/09/2005	10	14	96	nd	nd	nd	470	1 200	1 600	E10 000	
					Zc	ne G I	London Av	e. Canal					
CD	mud	10/03/2005	3.6	220	840	64	180	100	6 400	340	800	E7 900	E38
G1	SS	10/03/2005	9.5	110	1 000	٠.			0 .00	690	2 700	E150 000	
G2 0-1	lk sed	10/10/2005	0.3	17	52	nd	E6.6	E1.4	570	<250	<50	E850	E0.36
G3 0-1	lk sed	10/10/2005	2.6	51	290	nd	33	5.3	1 100	<250	640	E5 600	E12
G4 0-2	lk sed	10/10/2005	1.9	35	170	nd	nd	nd	450	<250	700	E4 200	
Other street mud and suspended sediment samples													
ONE	mud	10/04/2005	1.5	22	180	E0.6	E5.3	E0.5	1 200	E160	840	E2 200	E12
H1	SS	09/21/2005	1.5	17	110	nd	nd	nd	14 000	E 100	040	E2 200	EIZ
CHL	SS	10/04/2005	4.4	17	320	nd	nd	40.4	980	2 100	4 800	E320 000	
JNK	SS	10/04/2005	2.5	1.7	520 50	nd	nd	nd	2 600	530	10 000	E26 000	
JIVIX	33	10/04/2003	2.5	1.7						550	10 000	L20 000	
Mid-lake reference site samples													
MID	lk sed	09/28/2005	1.9	27	130	nd	nd	nd	650	_330	970	2 700	E0.05
MID	lk sed	10/04/2005	1.8	28	140	nd	nd	nd	120	E150	470	3 000	nd
MID	lk sed	10/20/2005	1.6	28	140	nd	nd	nd	150	E130	190	3 500	nd

^a Sample types are as follows: mud = street mud, ss = suspended sediment, and lk sed = surficial bottom sediment from Lake Pontchartrain. E = estimated (quantified but below long-term method reporting level). Nondetections (nd) are at variable reporting levels and were treated as zero in all summations. ΣDDT is the sum of p'p-DDT, p'p-DDD, and p'p-DDE. ΣPCBs is the sum of PCB Aroclors 1016/1242, 1254, and 1260. Σchlor is the sum of cis-chlordane, trans-chlordane, and trans-nonachlor. Σfipronil is the sum of fipronil, fipronil sulfide, fipronil sulfone, and desulfinylfipronil. Blank fields=constituent not measured.

atomic absorption spectroscopy (AAS), Se by hydride generation AAS, and As and Sb by hydride generation ICP—AES. Hg was analyzed on a separate digestate by cold vapor AAS. Total and organic carbon and total nitrogen were determined by combustion using a carbon/nitrogen analyzer.

PAHs, organochlorine pesticides, and PCBs were extracted, isolated, and quantified using U.S. Geological Survey (USGS) methods (13, 14). Following centrifugation, sediment was extracted in a Soxhlet apparatus overnight, split into two aliquots, and cleaned up by gel permeation chromatography (GPC). The first aliquot was analyzed for 19 parent PAHs and alkylated 2-5-ringed PAHs by gas chromatrophy/ mass spectrometry (GC/MS). The second GPC aliquot was split during combined alumina/silica adsorption chromatography with Florisil adsorption chromatography applied to the second fraction. Both fractions were analyzed by dual capillary-column gas chromatography/electron capture detection (GC/ECD) for the determination of organochlorine pesticides and PCBs. PCBs were quantified as individual Aroclor equivalents (1016/1242, 1254, or 1260) and as 27 specific congeners. For these and other organic compounds, a value that is below the long-term method reporting level but was quantified by the analyst is identified as "estimated" (13, 14) (Table 1).

Current-use pesticides were determined in wet sediment samples extracted with acetone in dichloromethane on an accelerated solvent extraction (ASE) system. The extract was passed through a graphitized carbon solid-phase extraction (SPE) column and eluted with a 50% solution of dichloromethane in ethyl acetate, then further cleaned up using

GPC. Sixty-three analytes were determined by GC/MS operated in the selected-ion monitoring mode using conditions described in (15-17).

UWI compounds (fragrances, detergent metabolites, selected PAHs, and other organic compounds) were determined using the procedure of Burkhart et al. (18). Wet bottom sediment was extracted twice using isopropanol/water mixtures on an ASE system and analyzed using capillary-column GC/MS. Sixty-one compounds were determined.

Laboratory quality assurance (data presented in ref 6) varied for the different chemical/analytical groups but in general consisted of the analysis of standard reference materials, duplicate environmental samples split at the laboratory, laboratory reagent spike samples, blank samples, and laboratory matrix spike samples, and the recovery of surrogate compounds.

Results and Discussion

Hurricane- and Pumping-Related Sediment Deposition. Field observations and radionuclide activities indicate extensive sediment redistribution during Hurricane Katrina

tensive sediment redistribution during Hurricane Katrina, the pumping of large amounts of turbid water into Lake Pontchartrain following the flooding, and the deposition of a new layer of sediment adjacent to the mouths of some canals. Extensive mud deposits left in some areas of New Orleans after the storms provide an obvious indication of sediment redistribution. In general, deposits were greatest in southeastern New Orleans (Chalmette and Ninth Ward neighborhoods (19)) and near the breach in the 17th Street Canal (mud deposits at site FDL were 30 cm or more thick).

Street-mud deposits in the Chalmette area were dominated by marine mud (19), consistent with the wetlands southeast of the city as the source of floodwater to this part of the city. Street-mud deposits on the north side of the city, where this study focused, probably were dominated by Lake Pontchartrain bottom sediment transported into the city through levee breaches. Contaminants associated with these deposits and with floodwaters pumped back into the lake could have been associated with bottom sediments prior to flooding; with historically contaminated soils, street dust, etc., in the city that mixed with flood sediments; or with contaminant sources inundated by the flooding.

17th Street Canal. During pumping on September 20, a plume of turbid water extended several hundred meters from the mouth of the 17th Street Canal into the lake. Sites E1-E3 were located within the plume, and site E4 was located about 200 m beyond the plume; suspended-sediment (sites E1 and E2) and bottom-sediment (sites E2-E4) samples were collected. Sediment texture transitioned from a 2-cm-thick soft, fine-grained organic-rich black sediment overlying a very firm layer (impenetrable using our samplers) at E2 and E3 (see photos in the Supporting Information, Figure SI-1), to an olive-gray silt-clay mixture sampled to 8 cm at E4. ⁷Be activities of 4.7 dpm/g (disintegrations per minute per gram) and 3.4 dpm/g at E2 and E3 indicated that the surface layers at these sites were recently deposited. Relatively constant activities of ⁷Be (1.8-2.7 dpm/g), ¹³⁷Cs, and excess ²¹⁰Pb to 4 cm at E4 indicated mixing of recent and older sediment. Sites MET, E2, and E3 are protected from longshore currents by a marina breakwater extending about 600 m into the lake, immediately east of the canal mouth (Figure 1), possibly enhancing deposition of fine-grained sediment. Recently deposited marine sediments sometimes can be distinguished by excess ²³⁴Th scavenged from seawater following the decay of dissolved U (11). Excess ²³⁴Th, however, was not detected in zone E samples and was detected in only one Lake Pontchartrain sample (C1), probably because of the combination of low salinity relative to seawater and a likely short residence time of sediments in the water column relative to the production rate of ²³⁴Th.

Other Canals. Deposition of recent sediment was less consistent in front of the other canals. Satellite images and direct observation indicated sediment plumes extending from the London Avenue and Jahncke Canals during September (Figure 1). Some sediment samples offshore from these canals had ⁷Be activities greater than about 3 dpm/g, indicating recent deposition, but many, including some samples close to shore and most samples west of the 17th Street Canal, were sandy and had very low ⁷Be activities (less than 0.5 dpm/g). Low ⁷Be activities off the west-side canals indicates that little or no new hurricane-related sediment was deposited.

Hurricane Rita. Samples collected pre- and post-Hurricane Rita (September 21 and October 9) indicated redistribution of lake sediment. At site E2, the sample collected after Hurricane Rita had a lower ⁷Be activity (1.2 dpm/g) than the pre-Rita sample (4.7 dpm/g), indicating remobilization of the layer of fine-grained sediment deposited after Hurricane Katrina. At site H2, activities of ⁷Be decreased from 3.3 dpm/g in the 0-0.5 cm sample to nondetections below 3 cm in the September 21, pre-Rita core, indicating a 1-2-cm layer of new deposition (Supporting Information Figure SI-2). In the October 9 core, 7Be was detected throughout the core indicating at least 21 cm of newly deposited sediment (possibly mixed with some older sediment). Excess ²¹⁰Pb in the post-Rita core also was nearly constant to 21 cm (3.0 \pm 1.1 dpm/g). These activities are too high to have resulted from the mixing of the pre-Rita surface layer with 20 cm of older sediment and indicate that Hurricane Rita remobilized and deposited a large amount of sediment at the site. The

site is in relatively deep water (14 m) off the mouth of the Industrial Canal, and could be a depositional basin for sediment mobilized by storms.

Sediment Chemistry. In addition to radionuclides, analytes from five major chemical groups were measured: elements, PAHs, chlorinated pesticides and PCBs, current-use pesticides, and UWI compounds (6). Selected constituents from each chemical group are presented for selected sites in Table 1. In general, concentrations were much higher in street mud and suspended sediments than in lake sediments, and concentrations among the lake bottom-sediment samples were highest near the 17th Street Canal.

Trace Elements and Nutrients. Concentrations of trace elements often are elevated in urban settings (20), and New Orleans is no exception (3, 19). In general, samples of street mud and suspended sediment and samples from the 17th Street Canal area had higher trace element and nutrient concentrations than samples in other media or from other locations (Table 1). In comparison to the mid-lake reference site (MID), all of the suspended sediment samples had elevated levels of nitrogen, phosphorus, and carbon, and some samples (E1, E2, G1) had elevated concentrations of Ag, Cu, Pb, and Zn. Cu, Pb, and Zn typically are elevated in street dust and have vehicular sources (21), suggesting urban nonpoint sources to floodwaters pumped from the canals. Elevated Ag might indicate wastewater contamination (22, 23). Suspended-sediment-associated concentrations had declined by October 3 at E1; water was flowing from the canal into the lake during sampling, but floodwater pumping had ceased. Among the bottom-sediment samples, only those collected near the 17th Street Canal (MET on September 29 and October 3; E2 on September 21 and October 9; E3 on October 9) contained elevated levels of trace elements (Cd, Cu, Pb, Zn, and Hg) relative to MID, except for elevated Ba at H2. Levels of these trace elements at E2 declined by October 9 but at E3 increased from September 21 to October 9. indicating sediment redistribution by Hurricane Rita. The samples farthest from shore in zones E and G (sites E4, E5, and G4) and most other lake sediment samples had relatively low trace element concentrations, similar to those from the mid-lake reference site (Table 1).

Previous studies of Lake Pontchartrain have shown similar distributions of trace elements. Overton (24) reported offshore decreases in Pb to background levels within 5-10 km from New Orleans in the early 1980s. Noakes (25) showed elevated Cu and Pb in bottom sediments off the 17th Street Canal in September 1996, but not in August 1997, suggesting contamination there is transient. He also reported elevated Ba, Cu, and Zn off the mouth of the Industrial Canal. Summarizing sediment data collected from 1990 to 1998, Manheim and Hayes (26) showed relatively elevated Ag, Cu, Hg, Pb, and Zn in Lake Pontchartrain bed sediments off the 17th Street Canal and, in some cases, the London Avenue and Industrial Canals, and elevated Ba off the Industrial Canal. In this study, Ba was elevated in both surficial and deeper samples at site H2 (mean of 1700 mg/kg, n = 11) compared with MID (mean of 480 mg/kg, n = 3). Elevated Ba has been identified previously in Lake Pontchartrain, including the area of site H2, and attributed to releases of drilling muds containing barium sulfate (26). Most elemental concentrations in surface and deeper samples decreased at H2 following Hurricane Rita, thus the large amount of sediment deposited by Rita apparently was not from contaminated sources.

 $\it PAHs.$ PAHs are ubiquitous in urban environments, and concentrations in sediment from many urban lakes and reservoirs across the United States have increased in recent decades (27). PAHs are useful tracers of urban effects because they are hydrophobic and persistent, and because concentrations in urban areas typically are 1-2 orders of magnitude higher than background concentrations.

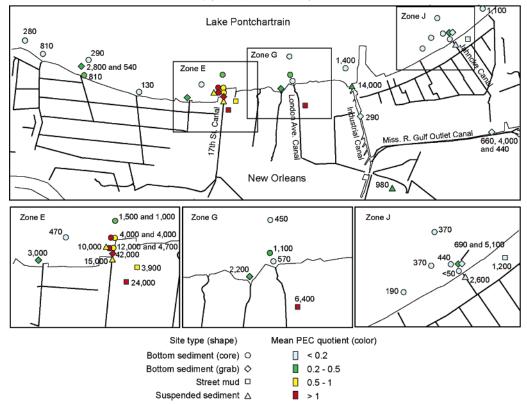


FIGURE 2. Concentrations of Σ PAH_{sqg} and ranges of values of mean PEC quotient for Lake Pontchartrain bottom sediments, suspended canal sediments, and street mud samples from New Orleans. The mean PEC quotient is the mean of the ratios of concentrations of individual constituents to their PEC (probable effect concentration) (28).

Concentrations of PAHs varied widely, and the highest concentrations occurred near the 17th Street Canal (Figure 2; ΣPAH_{SOG} is the summation used for the probable effect concentration (PEC) SQG of ref 28). PAHs were relatively high in suspended-sediment samples from the 17th Street and Industrial Canals, demonstrating transport of PAHs from the city to the lake. The highest concentration of ΣPAH_{SQG} in street mud was in sample FDL (Table 1). Concentrations of benzo[a]pyrene in all samples of street mud collected for this study (85-2400 µg/kg) exceeded the U.S. Environmental Protection Agency Region 6 human health screening level of $62 \mu g/kg$ for direct exposure pathways of residential soil (29). Median benzo[a] pyrene concentrations in soils collected near residential streets (141 μ g/kg), busy streets (255 μ g/kg), and open areas (144 µg/kg) before Hurricane Katrina also exceeded the screening level (3); concentrations in some specific urban sources, however, such as dust from parking lots treated with coal-tar sealcoat, greatly exceed those in post-Katrina street muds and New Orleans soils (range 72 000-820 000 μ g/kg) (30).

In Lake Pontchartrain bottom sediments, there is a relation between PAH concentrations and the recent deposition of sediment offshore from the canals. Samples from zone E had ΣPAH_{SOG} concentrations that decreased from 42 000 μg/ kg at MET at the mouth of the 17th Street Canal to $470 \,\mu\text{g/kg}$ at E5, the site farthest from the canal (Figure 2). The highest ΣPAH_{SOG} concentration in lake samples other than from zone E was 5100 μ g/kg, off the Jahncke Canal (zone J), although all other samples from zone J had very low concentrations. Although the ΣPAH_{SOG} concentration was moderately high in suspended sediment at H1 (Industrial Canal), concentrations in bottom sediment at H2 were quite low. A similar pattern of elevated PAH concentrations offshore from the 17th St. Canal, but not for the other areas along the New Orleans shoreline or the lake was shown by Manheim and Hayes (26) in samples collected in 1996.

The dominant sources of PAHs in samples collected for this study are pyrogenic. Combustion produces mostly higher molecular weight (4-7-ringed) parent PAH, whereas uncombusted fuels and organic matter contain more lower molecular weight PAH and their alkylated homologues. The ratio of 2- and 3-ringed PAH plus homologues to 4- and 5-ringed parent PAH (2 + 3/comb) indicates the relative dominance of pyrogenic (ratios less than about 1) or petrogenic PAH (31). The median 2 + 3/comb ratio among all samples collected in this study was 0.38 and among samples with ΣPAH_{SOG} greater than 2000 $\mu g/kg$ was 0.53, values indicative of pyrogenic sources and typical of U.S. urban lake sediments (27). Only one bottom-sediment or street-mud sample had a value greater than 1 (1.3 in CD). The PAH ratios thus suggest that spilled fuels played a very limited role in PAH contamination of the sediment samples collected by this study.

Organochlorine Pesticides and PCBs. The occurrence of organochlorine pesticides and PCBs followed the same general spatial pattern as the PAHs. The most frequently detected of this group of compounds were p,p'-DDD, p,p'-DDE, dieldrin, cis-chlordane, trans-chlordane, trans-nonachlor, and PCBs. The highest concentrations were at zone E sites, with lower concentrations near the London Avenue and Industrial Canals and mostly nondetections in samples collected farther from shore (Table 1; ref 6). The bottomsediment samples from E3 (September 21) and from MET (September 29) had particularly high concentrations of some compounds; however, the post-Rita sample from E3 (October 9), had much lower concentrations than the pre-Rita sample. Nondetections were reported for most constituents in suspended-sediment samples because of small sample masses and high detection levels. Concentrations in streetmud samples were variable, with mostly nondetections at site ONE, but some relatively high concentrations at CD and FDL (e.g., 12 and 27 μ g/kg, respectively, of dieldrin).

Current-Use Pesticides. Thirteen of the 63 compounds analyzed were detected at least once. Among these, chlorpyrifos and three fipronil degradates (fipronil sulfide, fipronil sulfone, and desulfinyl-fipronil) were detected in 40% or more of the samples. Parent fipronil was detected in 25% of samples. About one-third of all detections were in streetmud samples; chlorpyrifos, fipronil, and three fipronil degradates were detected in all four street-mud samples. Similar to concentrations of other contaminants, the highest concentrations of current-use pesticides in lake bottomsediment samples were at zone E sites, but similar concentrations also were in samples G3 (Table 1) and J4. Both chlorpyrifos and, more recently, fipronil have been applied in New Orleans for control of termites, as well as other insects. Permethrins, also used to control termites, were not detected in any samples in this study (interferences caused reporting levels to be raised for some samples), but were detected in 38% of the street-mud samples from another post-Katrina study (19) at concentrations as high as 1100 μ g/kg (W.T. Foreman, U.S. Geological Survey, written communication, 2006). Detections of other parent (atrazine, carbaryl, dacthal, dieldrin, trifluralin) or pesticide degradate compounds likely are related to current or historical urban pesticide applications (32) and sediment organic carbon/water partition coefficients (log K_{oc} s) of 2 or greater (33, 34).

Neither national benchmarks nor SQGs are available to put these results into a larger context. Nowell et al. (32) reported detection frequencies for these parent pesticides (except fipronil) from 0 (carbaryl) to 40% (dieldrin) from a survey of bed-sediment studies in the United States. Yu and Cole (35) reported atrazine concentrations in Lake Pontchartrain bed sediments of 4.0–41 μ g/kg for samples collected in 1992 offshore from the mouth of the Duncan Canal (near site B1, Figure 1). Current-use pesticides were not measured in sample B1, and atrazine was not detected at nearby sites A1, C1, C2 (reporting level 1–1.4 μ g/kg). Atrazine was detected at ELM (0.24 μ g/kg estimated) and in one sample each from three other sites, ITC, MID, and J4 (range 1.3–2.6 μ g/kg), all sampled post-Hurricane Rita.

Urban Waste Indicators. The UWI analytical method measures a diverse suite of organic compounds that reflects urban nonpoint source and wastewater inputs to surface waters (36); methods for UWI analysis in sediment were developed only recently (18). The compounds measured fall into four general groups: PAHs, fecal and sewage indicator compounds, industrial chemicals, and pesticides and other household chemicals.

Sixteen of the 61 compounds reported were detected in 50% or more of samples, including parent and methyl substituted PAHs (fuels, combustion, parking-lot sealants), anthraquinone (natural sources, dye production, pulp and paper industry, bird repellent), indole (coal tar, pesticide inert ingredient, fragrance in coffee), 3-methyl-1H-indole (fragrance, stench in feces, coal tar), para-cresol (wood preservative), cholesterol (animal and plant sterol; often used as a fecal indicator), and beta-sitosterol and beta-stigmastanol (plant sterols). Phenol (phenolic and epoxy resins and other synthetic manufacturing, disinfectant) was detected in 43% of samples and bis(2-ethylhexyl) phthalate (plasticizer for polymers and resins) was detected in 45% of samples; both were reported in one or more Katrina floodwater samples (37). Detection frequency was less than 17% for all other compounds except carbazole (39%), bisphenol A (29%), and 3-beta-coprostanol (37%), a fecal steroid that is generally a strong indicator of human or animal wastewater sources and that was detected in 85% of U.S. streamwater samples (36).

In most cases, suspended-sediment samples had much higher concentrations of the UWI compounds than bed-sediment and street-mud samples (Table 1), indicating transport of UWI compounds to the lake by floodwaters.

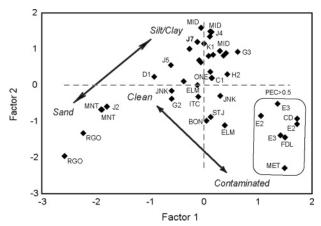


FIGURE 3. Factor analysis scores for sediment samples from Lake Pontchartrain and New Orleans canals and streets.

Among the Lake Pontchartrain samples, the patterns of high and low concentrations for trace elements, PAHs, and organochlorine compounds did not occur for some of the UWI compounds. In zone E, for example, the highest concentrations of cholesterol (Table 1), phenol, and *beta*-stigmastanol (6) were at E5, which had the lowest concentrations of Pb, Zn, PAHs, and organochlorine compounds. These differences likely reflect differences in sources (e.g., release of untreated wastewater from flooded sewers and treatment plants) and in how these UWI compounds were transported and accumulated in sediment.

Natural and Anthropogenic Effects on Sediment Chemistry. Because a large number and variety of constituents were measured, factor analysis was used to detect underlying structure in the data set (38). The factor analysis included 42 samples. The selected variables were those constituents that were detected frequently, are recognized as contaminants, and (or) represent relatively unique sources or chemical behaviors. Current-use pesticides were excluded because of few data. Most variables were reasonably represented by a log-normal distribution, so logarithms of values were used. Nondetections were replaced with values below the lowest reporting level.

A principal components analysis of the covariance matrix was performed; the first three factors explained 79% of the variance in the data. Factor 1 explains 58% of the variance and is heavily weighted by common anthropogenic contaminants, including trace elements (especially Cu, Pb, and Zn), PAHs, and organochlorine compounds (Supporting Information, Table SI-1). It also is heavily weighted by the UWI compounds anthraquinone, cholesterol, beta-sitosterol, and indole. Factor 2 accounts for 15% of the variance and is positively weighted by most elements, particularly those less heavily weighted by factor 1 (Cr, Li, and Ni), and negatively weighted by chlorinated hydrocarbons, carbozole, and diethylhexyl phthalate. Factor 3 accounts for 6% of the variance and is positively weighted by phenol and para-cresol and negatively weighted by Ba.

The environmental interpretation of the factors is made clearer by plotting scores for the first two factors (Figure 3). Samples with elevated concentrations of trace elements, PAHs, chlorinated hydrocarbons, and many of the UWI compounds have large positive factor 1 scores and large negative factor 2 scores (Supporting Information, Table SI-2). All samples that have mean PEC quotients greater than 0.5, an indication of expected adverse effects on benthic biota (28), are in this group. The only sample in this group not from near the 17th Street Canal is the street-mud sample CD from near the London Avenue Canal. Variation from the lower-left quadrant to the upper middle of the graph (Figure 3) is explained primarily by natural variations in sediment



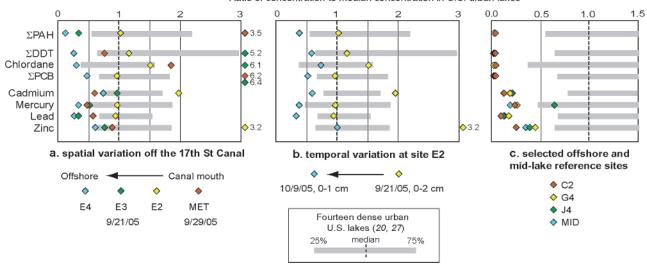


FIGURE 4. Comparison of selected Lake Pontchartrain bed-sediment samples to median concentrations in U.S. urban lakes (20, 27)

surface area and organic carbon concentration. Samples with small factor 1 scores and positive factor 2 scores tend to be fine grained and relatively free of anthropogenic contaminants. This group includes many samples offshore from canals other than the 17th Street Canal and the mid-lake reference site. Samples with negative factor 1 and factor 2 scores are sandy and also are relatively free of anthropogenic contaminants. Because of their smaller surface area, the sandy samples tend to have lower trace element concentrations than more clayey samples (e.g., Pb and Zn at RGO and MNT as compared to MID; Table 1). Thus, the factor analysis indicates that urban contaminant sources and natural variations in bulk sediment properties are responsible for most variations in sediment chemistry of these Lake Pontchartrain samples.

Comparison to U.S. Urban Lakes and Sediment-Quality Guidelines. Concentrations of selected constituents in sediments from New Orleans and Lake Pontchartrain were put into a larger context by comparing them to concentrations measured in other urban lakes. Concentrations measured in this study were normalized to median concentrations measured in sediments from 14 urban lakes (50% urban land use or greater) located across the United States (20, 27). All these urban lakes are smaller, their watersheds are more densely urbanized, and they do not have the circulation of an estuary like Lake Pontchartrain, so they are expected to have higher levels of contamination. The highest concentrations measured in Lake Pontchartrain are similar to (E2, most constituents) or higher than (MET; E3; Zn and Cd at E2) median concentrations in the urban lakes (Figure 4a). The concentrations of chlorinated hydrocarbons at E3 in September are 5-6 times the urban medians, and PAHs and PCBs at MET are 3-6 times the urban medians. However, the offshore decrease is rapid and at site E4 levels are less than the 25th percentile concentration of the urban lakes.

Sites E2, E3, and E4 were sampled again on October 9, following Hurricane Rita, and constituent levels at E2 decreased by about one-half (Figure 4b). At site E3, concentrations of chlorinated pesticides and PCBs also were much lower than in the sample collected earlier, although PAH and most trace element concentrations remained about the same and Zn and some UWI compound concentrations increased (Table 1). The large temporal changes at E2 and E3 indicate sediment redistribution by Hurricane Rita.

PAH and chlorinated hydrocarbon concentrations in most other Lake Pontchartrain samples were well below national urban medians (Figure 4c) and comparable to concentrations in undeveloped reference lakes sampled by the USGS in other parts of the country (20, 27). Sites C2, G4, and J4 are $1.5-2~\rm km$ from shore and in front of major canals, yet concentrations are similar to the mid-lake reference site (Figure 4c). $\rm \Sigma PAH_{SQG}$ concentrations at these four sites (120–650 $\mu g/kg$) are typical of those in remote reference lakes, and no chlorinated hydrocarbons were detected. Trace element concentrations also are typical of those in remote reference lakes.

To assess overall sediment quality relative to potential toxicity to benthic biota, the mean PEC quotient was computed (28). MacDonald et al. (28) determined that sediment with a mean PEC quotient greater than 0.5 was 85% likely to have adverse effects on benthic organisms and greater than 1.0 was 92% likely to have adverse effects on benthic organisms. Ten of the 44 samples (23%) collected in this study for which mean PEC quotients could be calculated were greater than 0.5, and five of those were greater than 1.0 (Figure 2). The only samples with mean PEC quotients greater than 0.5 were street-mud sample CD and samples from near the mouth of the 17th Street Canal. The highest mean PEC quotients were 3.2 (E3 on September 21, before Rita) and 2.2 (MET on September 29, after Rita). The low mean PEC quotients for the other samples and the overall distribution of quotients indicates the limited spatial extent of urban and hurricane-related effects on Lake Pontchartrain (Figure 2). Thus, except for a small area within a few hundred meters of the 17th Street Canal, sediments in Lake Pontchartrain were cleaner than is typical of other U.S. urban lakes, and substantial adverse effects on aquatic life are unlikely.

The results of this study indicate that relatively contaminated sediment was discharged from New Orleans into Lake Pontchartrain by pumping of floodwaters, but that deposition of contaminated sediment in Lake Pontchartrain was spatially and possibly temporally limited. These conclusions are consistent with those from studies prior to Hurricane Katrina (e.g., 5, 25, 26). The relatively high concentrations of urbanrelated contaminants measured in sediment samples collected offshore from the 17th Street Canal during this and other studies could be the result of the periodic discharge of urban stormwater from the canal and the location of a marina breakwater. Because the breakwater provides some protection from currents at this site, redistribution might occur only during major storms, allowing for more persistent deposition of fine-grained sediments discharged from the canal. Transport of fines from the other canals as a result of longshore currents might explain why contaminant concentrations in bed sediments off the mouths of the other canals generally are low.

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Supporting Information Available

Additional tables and figures illustrating soil sediments and further details about this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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